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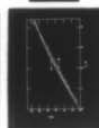
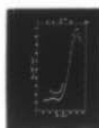
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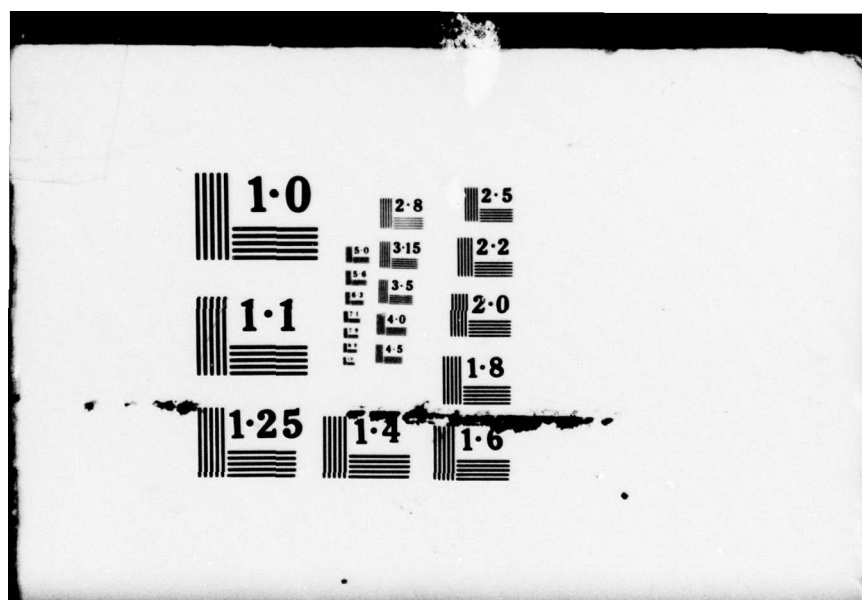
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The Effect of Intercluster Interactions on the Thermal and Magnetic Properties of $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl} \cdot 6\text{H}_2\text{O}$

by

James T. Wroblewski, Chester T. Dziobkowski, and David B. Brown

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Excellent agreement between experimental and theoretical heat capacities is found when two crystallographically inequivalent pairs of equilateral trimer sites with different intercluster exchange parameters are assumed. Low-temperature magnetic susceptibility data for this complex are well reproduced by using the parameters which are obtained from the heat capacity data. ✓

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The Effect of Intercluster Interactions on the Thermal and Magnetic Properties of $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 6\text{H}_2\text{O}$

James T. Wroblewski, Chester T. Dziobkowski, and David B. Brown
Department of Chemistry, University of Vermont, Burlington,
Vermont 05405

Inclusion in the hamiltonian of a perturbing term which describes the pairwise spin exchange between $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$ equilateral triangular clusters in $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 6\text{H}_2\text{O}$ splits the unperturbed ground state into two nondegenerate Kramers doublets. The effect of this splitting is to introduce a Schottky type anomaly in the theoretical heat capacity curve. Excellent agreement between experimental and theoretical heat capacities is found when two crystallographically inequivalent pairs of equilateral trimer sites with different intercluster exchange parameters are assumed. Low-temperature magnetic susceptibility data for this complex are well reproduced by using the parameters which are obtained from the heat capacity data.

Previous theoretical models¹⁻⁶ proposed to account for the low-temperature thermal and magnetic susceptibility behavior of $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 6\text{H}_2\text{O}$ are based on physically unsubstantiated assumptions. These assumptions derive from a necessity to lift the degeneracy of the two Kramers doublets which comprise the ground spin level. Although the C_{2v} (isosceles triangle) model of Kambe which is given by

$$\underline{H} = \underline{J}_0(\underline{S}_1 \cdot \underline{S}_2 + \underline{S}_1 \cdot \underline{S}_3) + \underline{J}_1(\underline{S}_2 \cdot \underline{S}_3), \quad (1)$$

where \underline{S}_1 , \underline{S}_2 , and \underline{S}_3 are spin operators, describes the low-temperature heat capacity data for this compound, direct evidence for a structurally-distorted Cr_3O cluster is not available. Furthermore, this model cannot simultaneously describe the magnetic susceptibility and heat capacity data for this compound. Alternatively Mishima and Uryu⁶ have recently calculated the magnetic heat capacity for this material based on the Dzyaloshinskii-Moriya exchange interaction given by

$$\underline{H} = \frac{iD}{2} \sum_{ij} (\underline{S}_i^+ \underline{S}_j^- - \underline{S}_i^- \underline{S}_j^+). \quad (2)$$

This "antisymmetric" exchange hamiltonian splits the ground state as required but fails to describe the magnetic heat capacity data of the chromium acetate complex. In actuality the Dzyaloshinskii-Moriya exchange interaction also requires a structurally-distorted Cr_3O cluster in order that $|D| \neq 0$. Finally, Uryu and Friedberg⁴ have calculated the magnetic susceptibility and heat capacity functions derived from an axial crystal field model given by

$$\underline{H} = \underline{H}_0 + \sum_{\underline{i}=1}^3 \underline{D}_{\underline{i}} [(\underline{S}_{\underline{i}} \cdot \underline{S}_{\underline{i}})^2 - 1/3 \underline{S}_{\underline{i}} (\underline{S}_{\underline{i}+1})], \quad (3)$$

where $\underline{H}_0 = \underline{J}_0 (\underline{S}_1 \cdot \underline{S}_2 + \underline{S}_2 \cdot \underline{S}_3 + \underline{S}_3 \cdot \underline{S}_1)$. In the same paper⁴ they also investigated the effect of inclusion in the hamiltonian of higher spin coupling terms given by

$$\underline{H} = \underline{H}_0 + \underline{J}' [(\underline{S}_1 \cdot \underline{S}_2)(\underline{S}_2 \cdot \underline{S}_3) + (\underline{S}_2 \cdot \underline{S}_3)(\underline{S}_3 \cdot \underline{S}_1) + (\underline{S}_3 \cdot \underline{S}_1)(\underline{S}_1 \cdot \underline{S}_2)]. \quad (4)$$

Whereas Eq. (3) is not a satisfactory description of the thermal and magnetic data for the chromium acetate complex, Eq. (4) is Hermitian only if an additional term of the type

$$\underline{J}' [(\underline{S}_3 \cdot \underline{S}_2)(\underline{S}_2 \cdot \underline{S}_1) + (\underline{S}_1 \cdot \underline{S}_3)(\underline{S}_3 \cdot \underline{S}_2) + (\underline{S}_2 \cdot \underline{S}_1)(\underline{S}_1 \cdot \underline{S}_3)] \quad (5)$$

is added to Eq. (4).⁷ The effect of this additional term is to restore the degeneracy of the two Kramers ground state doublets.⁵

In view of the apparent failure of the above models to describe the properties of the chromium acetate trimer and because of our initial success in modeling the low-temperature magnetic susceptibility data for similar Fe(III) trimers⁸ with an intercluster spin exchange model, we felt it would be appropriate to consider the possible influence of such a model on the properties of the chromium compound. We took as our hamiltonian

$$\underline{H} = \underline{J}_0 (\underline{S}_1 \cdot \underline{S}_2 + \underline{S}_2 \cdot \underline{S}_3 + \underline{S}_3 \cdot \underline{S}_1) + \underline{J} (\underline{S}_{\underline{A}} \cdot \underline{S}_{\underline{B}}), \quad (6)$$

where $\underline{S}_{\underline{A}}$ and $\underline{S}_{\underline{B}}$ are spin operators which couple cluster A with cluster B. Basis spin levels $\underline{S}_{\underline{iA}}$ and $\underline{S}_{\underline{iB}}$ were assumed to be the unperturbed spin vectors of the individual trimeric Cr_3O clusters. This analysis results in a 128-fold degenerate six-spin problem.

The effect of the hamiltonian given by Eq. (6) is to split the ground state into two Kramers doublets separated by $2j$. The first unperturbed excited state is split into four spin levels with $12j$ total separation. Although only the lowest few of the 30 spin levels which result from Eq. (6) contribute to the low temperature limiting form of the appropriate partition function, we found it no less convenient to include all levels in the ensuing calculations.

Heat capacities for $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 6\text{H}_2\text{O}$ obtained by Sorai et al.⁵ and by Wucher and Wasscher² were independently fit to the heat capacity expression for Eq. (6). Because there is substantial disagreement between the two data sets we have chosen the more complete set of Sorai et al. to serve as a more critical test of our model than the limited set of Wucher and Wasscher. Lattice heat corrections were applied to the experimental \underline{C}_V as

$$\underline{C}_V^D = 523.9718 \chi_0^{-3} \int_0^{\chi_0} [\underline{x}^4 \underline{e}^{\underline{x}} / (\underline{e}^{\underline{x}} - 1)^2] d\underline{x} \quad (7)$$

for the Debye heat capacity, where $\underline{x}_0 = 120/T$,² and

$$\underline{C}_V^E = 54R \underline{y}_0^2 [\underline{e}^{\underline{y}_0} / \underline{e}^{\underline{y}_0} - 1)^2] \quad (8)$$

for the Einstein heat capacity, where $\underline{y}_0 = 270/T$ and R is the gas constant. The magnetic heat capacity, \underline{C}_m , was obtained as

$$\underline{C}_m(\text{obsd}) = \underline{C}_p(\text{obsd}) - \underline{C}_V^D - \underline{C}_V^E. \quad (9)$$

The experimental values of \underline{C}_m were fit to Eq. (6) by using the Simplex optimization algorithm.⁹ Figure 1 compares the data

of Sorai et al.⁵ (open circles) and Wucher and Wasser² (full circles) with best fit curves calculated by Eq. (6). In order to adequately describe the low-temperature heat capacity data of Sorai et al. it was necessary to consider the presence of two different equilateral Cr₃O trimer sites having distinct values of j . A distribution function of the type

$$C_m(\text{calcd}) = zC_m(J_o, j_1) + (1-z)C_m(J_o, j_2) \quad (10)$$

was employed. Parameters $J_o = -35k$, $j_1 = +0.9k$, $j_2 = +3.6k$, and $z=0.80$, where k is Boltzman's constant, were obtained for the 1-6K data of Sorai et al. The C_m curve calculated with these values is shown in Fig. 1. Data of Wucher and Wasscher were well described with $J_o = -44k$, $j_1 = +1.5k$, $j_2 = 0.0k$, and $z=1.0$.

In order to test the validity of these parameters, the magnetic susceptibility data of Schriempf and Friedberg³ were modeled with parameters obtained from fitting the heat capacity data of Sorai et al. Results of this calculation are shown in Fig. 2. The experimental susceptibilities are reproducible to $\pm 3\%$, an accuracy within the quoted experimental uncertainty.³

The mechanism for intercluster spin exchange is undoubtedly associated with the hydrogen bonding between trimer centers. The hydrogen bonding network in crystals of $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$ involves carboxyl oxygens, lattice water molecules and chloride ions.¹⁰ Because of the observed¹⁰ room-temperature disorder of the lattice water and halide sites we would anticipate several possible types of intertrimer spin-exchange pathways in this material. It is however, not possible to make an a priori

statement about the number and magnitude of these pathways based on current data. A finite value of z however indicates that two or more intercluster exchange pathways are available at low temperatures in this material.

We believe that the intercluster model proposed above provides a physically realistic basis for understanding the properties of numerous similar cluster compounds. We propose that such a model be applied as a perturbation to the normal Heisenberg spin exchange model in those cases in which models such as Eqs. (1) - (4) are not substantiated by direct physical measurements.

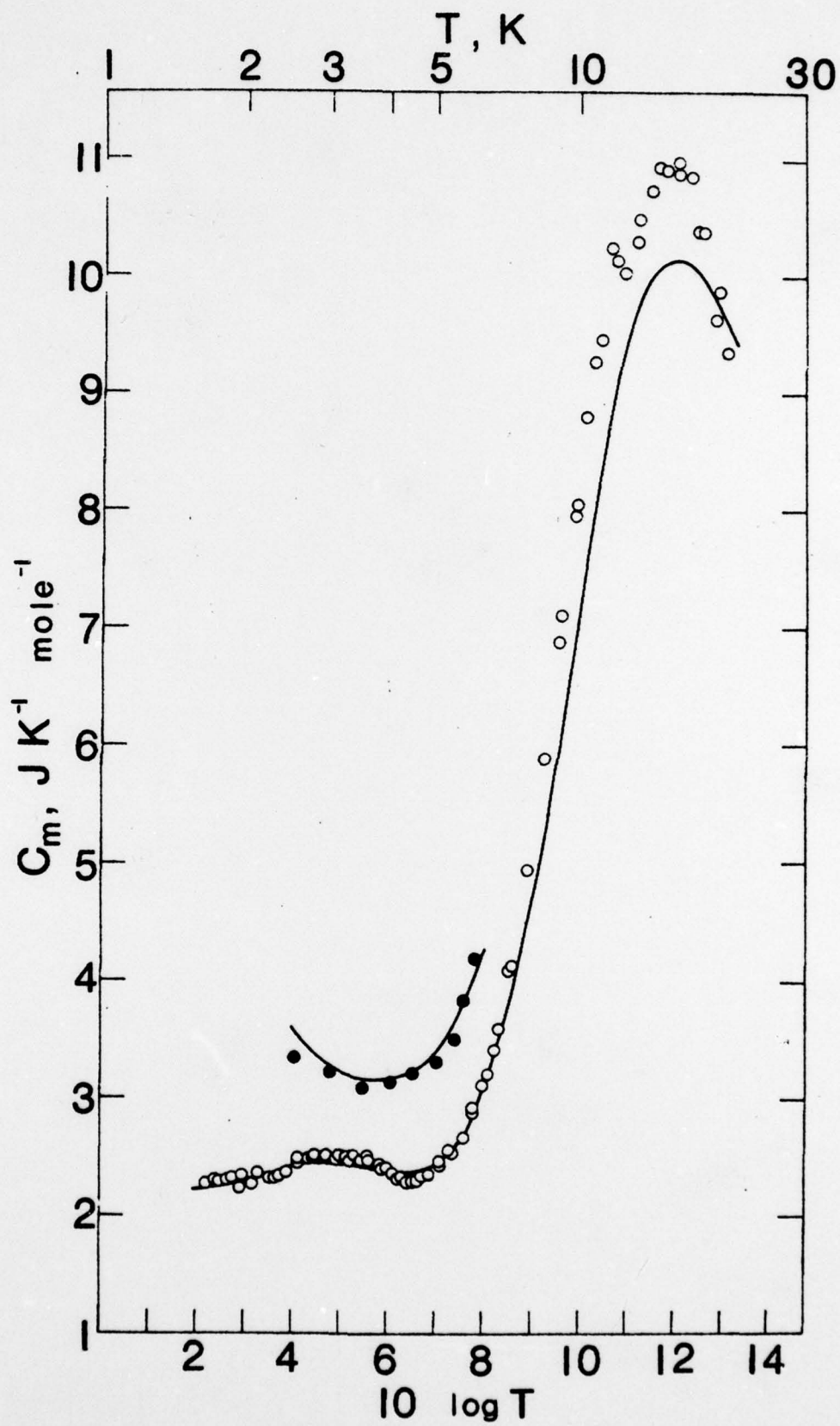
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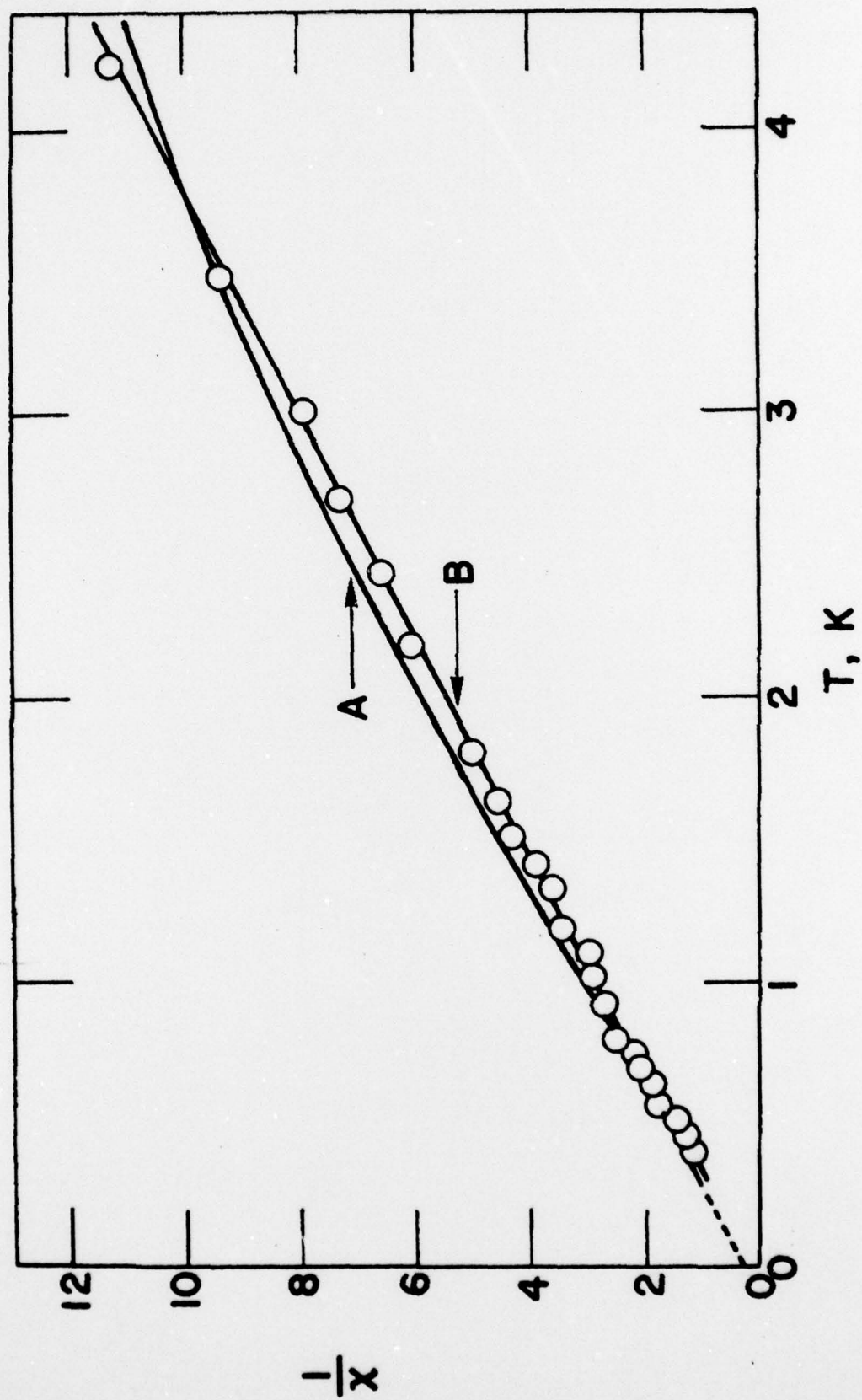
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Figure Captions

Fig. 1. Magnetic heat capacity of $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})]\text{Cl}\cdot 6\text{H}_2\text{O}$ versus $10 \log T$. Data of Sorai et al.⁵ (O) fit to curve A with parameters given in the text. Data of Wucher and Wasshcer² (●) fit to curve B with parameters given in the text.

Fig. 2. Reciprocal magnetic susceptibility versus T .³ The smooth curve A represents the intercluster fit with parameters given in the text. Curve B represents the Curie-Weiss law fit with $C = 0.393$ and $\theta = -0.13\text{K}$.





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